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Chloride diffusion model in concrete in marine environment with considering binding effect

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Abstract - This paper presents a new chloride diffusion model in concrete exposed to marine environment, which considers the individual effects of different types of chloride binding. The present model has following new features. (1) The bound chlorides are divided into two types. One is reversible, which is related to the physical binding, and the other is irreversible, which is related to the chemical binding. (2) The reversible bound chloride remains its charge and continues to provide its driving force to influence the movement of free chloride ions. (3) The governing equation for the mass conservation of chlorides is established on the framework of representative elementary volume of concrete and thus the diffusion coefficient used in the present model is consistent with the effective diffusion coefficient defined in the steady-state diffusion tests of chloride in concrete.

Keywords – Modelling; chloride diffusion; ionic binding; chemical potential; concrete; marine environment.

1. Introduction

Metal corrosion induced by chlorides is a major problem of structures in marine environment [1,2,3]. For concrete structures exposed to marine environment chlorides can also penetrate through the concrete cover to induce the corrosion of reinforcing steel and thus deteriorate the reinforced concrete structures. The understanding of the transport mechanism of chlorides in concrete is fundamental for the prediction of the service life of reinforced concrete structures. Concrete is a porous material. The transport of chlorides in concrete involves not only the diffusion of chloride ions in pore solution but also the physical and chemical interactions between chloride ions and pore surfaces within cement matrix [4,5]. The latter provides a "binding" function to mobile chloride ions. The capacity of concrete cementitious system to bind chloride ions has an important effect on the rate of chloride transport in concrete and thus also on the corrosion initiation of reinforcing steel in reinforced concrete structures [6,7]. With increasing use of concrete in offshore and marine structures a better understanding of the transport mechanism of chlorides in concrete becomes even more important.

Chloride binding in concrete is a complicated matter. The binding mechanism involves physical adsorption and chemical reactions. Numerous studies have been conducted on chloride diffusion in concrete with considering the chloride binding effect. For example, Page and Vennesland [8] experimentally investigated the chloride binding capacity of silica fume cement pastes. It was found that the partial replacement of Portland cement by increasing percentages of silica-fume leads to a regular decrease in alkalinity of the pore solution and a reduction in the chloride binding capacity of the material. Arya et al. [9] investigated the chloride binding in concrete by analysing pore solution expressed from cement paste specimens using a pore press. It was found that, for chlorides introduced at the time of mixing, cement type, the type and proportion of cement replacement material, the chloride salt and total chloride content are the most important factors governing the chloride binding, whereas the water/cement ratio and curing time prior to immersion have little effect on the chloride binding. Zhang and Gjørv [10] presented an analysis of the diffusion behaviour of chlorides in concrete. It was shown that for stronger ionic solutions ionic interaction could reduce the chemical potential and thus the driving force of the diffusing species. In addition, the electrical double layer forming on the solid surface and the chemical binding could also significantly interfere the transport of chloride ions. Glass et al. [11] examined the method of obtaining chloride binding data from steady-state diffusion experiments by using the measured total chloride profile and estimated free chloride profile. Tang and Nilsson [12] carried out an experimental study on chloride binding capacity and binding isotherms of ordinary Portland cement pastes and mortars with water/cement ratios 0.4, 0.6 and 0.8. It was shown that the chloride binding capacity of concrete is strongly dependent upon the content of CSH gel in the concrete, regardless of water/cement radio and the addition of aggregate. The relationship between the bound and free chlorides can be modelled by using a Freundlich isotherm at high free chloride concentrations and a Langmuir isotherm at low free chloride concentrations. Sandberg [13] presented an experimental investigation into chloride binding in concrete and the effect of hydroxide leach on the chloride binding. Boddy et al. [14] provided the sensitivity study of multi-mechanistic chloride transport model, which considers the multi-mechanistic transport, chemical binding, and time-dependent nature of concrete properties. Jensen et al. [15] examined the influence of paste and exposure parameters on chloride ingress in cement pastes by using electron-probe microanalysis techniques. The measured results were analysed using Fick's law modified by a term for chloride binding. It was shown that the inclusion of chloride binding significantly improves the profile shape of the modelled ingress profiles. Martín-Pérez et al. [16] examined the impact of using different binding isotherms on time-dependent chloride penetration profiles in concrete specimens submerged in seawater and exposed to de-icing salts. Glass and Buenfeld [17] presented a study on the influence of chloride binding on the chloride-induced corrosion risk in reinforced concrete structures. Baroghel-Bouny et al. [18] presented a method for predicting chloride binding isotherms of concrete by using analytical model and/or numerical inverse analysis method. Li and Shao [19] examined the effect of four different chloride binding isotherms on the service life of RC pipe piles exposed to marine environments. Yoon et al. [20] provided a feasibility study of using calcined layered double hydroxides to prevent chloride-induced deterioration in reinforced concrete. It was demonstrated that the calcined layered double hydroxides not only adsorbed chloride ions in aqueous solution with a memory effect but also had a much higher binding capacity than

originally layered double hydroxides in the cement matrix. Tang [21] presented a simplified method of applying the ClinConc model to predict both the free and total chlorides in concrete by modelling the transport of free chloride ions using free chloride diffusion potential and then calculating the total chlorides by taking into account chloride binding. Andrade et al. [22] proposed an electrical resistivity model for the calculation of the retardation factor to take into account the effect of bound chlorides on chloride diffusion. In addition, the effects of micro- and macro-cracking [23] and concrete hetero-organisation [24] on the penetration of chlorides in concrete have been also investigated using numerical methods and/or experimental methods.

The above survey of literature shows that, despite the considerable amount of work published in literature on chloride binding and its effect on chloride transport in concrete exposed to marine environment, there is very little research focussing on the individual effects of different types of bound chlorides on chloride transport in concrete. In this paper, a new chloride diffusion model is developed, in which the bound chloride is divided into two types. One is reversible, which is related to the physical binding. The other is irreversible, which is related to the chemical binding. These two types of bound chloride are treated separately in the present model. In addition, it is assumed that the reversible bound chloride remains its charge and thus can also provide the driving force to influence the movement of free chloride ions. Finally, the governing equation for the mass conservation of chlorides is established based on the unit volume of representative elementary concrete and thus the diffusion coefficient used in the present model is consistent with the effective diffusion coefficient of chloride ions defined in the steady-state diffusion tests of chlorides in concrete.

2. Fickian diffusion model considering ionic binding

Chloride diffusion in concrete is usually described by using the Fick's second law as follows [25],

$$\frac{\partial C}{\partial t} = \nabla(D_a \nabla C) \tag{1}$$

where C is the total chloride content in concrete, normally expressed as the mass of chlorides in the unit mass of binder or concrete, D_a is the apparent diffusion coefficient of chlorides in concrete which includes the effect of chloride binding, and t is the time. If the diffusion coefficient, initial and boundary conditions of chlorides are known then the total chloride content at any time at any place in a concrete can be predicted using Eq.(1). The main advantage of using Eq.(1) is its simplicity. The drawback of using Eq.(1) is the difficulty in defining the boundary condition of chlorides because the total chlorides expressed as percentage by mass of binder or concrete is different from the chlorides in the exposed environment that are normally defined by using the chloride concentration in solution. Also, since it is only the free chloride that is harmful to the reinforcement it is preferable to know the free chloride content in concrete. By splitting the total chlorides into free and bound chlorides and considering the fact that the bound chloride is not able to transport, the following mass conservation equation of chlorides based on the unite volume of concrete, which is similar to Eq.(1), can be established [26,27,28,29],

$$\frac{\partial C_f}{\partial t} + \frac{\partial C_b}{\partial t} = \nabla\left(D\nabla C_f\right) \quad (2)$$

where C_f and C_b are the free and bound chlorides in the unit volume of concrete, respectively, D is the diffusion coefficient of chlorides in concrete, which is different from D_a in Eq.(1) because it excludes the effect of chloride binding [30,31]. Note that different formats have been used in literature for defining the rates of change of free and bound chlorides described by the left-hand-side terms of Eq.(2). Some of them are related to concrete porosity or the volume fraction of liquid phase of concrete [16,17,30,31]. This, however, is purely due to the use of different definitions and/or units for the free and bound chlorides. In order to solve Eq.(2) for C_f, one has to know the relationship between the free and bound chlorides, that is so-called chloride binding isotherms [18,32,33]. Nevertheless, once the bound chloride is expressed in terms of the free chloride, Eq.(2) can be used to predict the transport of free chloride in concrete.

Eq.(2), or its similar form, has been widely used in literature for predicting the penetration of chlorides in concrete and determining the service life of reinforced concrete structures exposed in chloride environment [16,17,26,27,28,29,30,31,34]. However, the behind assumptions used in developing this equation have not been discussed or justified. First, the use of Eq.(2) together with an analytical chloride binding isotherm means that the chloride binding is completely reversible. This seems contradictory to some of chloride binding mechanisms, for example, the formation of Friedel's salt [33,35,36], which is not reversible. Secondly, the flux of free chloride calculated in Eq.(2) is purely based on the concentration gradient of free chloride ions. This seems not consistent to the flux calculated based on the chemical potential gradient of all chloride ions including those physically bound on the concrete pore surface. The latter will be discussed in more detail in following section.

3. Modified diffusion model considering ionic binding

In order to consider the irreversible process of chemically bound chlorides, the bound chloride is now divided into two parts [18]. One is irreversible, which is due to the chemical binding of chlorides. The other is reversible, which is due to the physical binding of chlorides. The former is modelled by using a sink term, whereas the latter is modelled using a chloride binding isotherm. Consider the mass conservation of chlorides in the representative elementary volume of a saturated concrete (see Fig.1). The change of the total chlorides in the volume is solely caused due to the flux difference of the free chloride pass through the surface areas of the representative concrete, as follows,

$$\frac{\partial C_f}{\partial t} + \frac{\partial C_{b2}}{\partial t} = -\nabla J - Q(C_{b1}) \quad (3)$$

where C_{b1} and C_{b2} are the irreversible and reversible bound chlorides, respectively, J is the flux of free chloride ions pass through the unit area of concrete in unit time, $Q(C_{b1})$ is the sink term which is the function of the irreversible bound chloride and can be assumed as follows,

$$Q(C_{b1}) = \frac{\partial C_{b1}}{\partial t} = k_b(\bar{C}_{b1} - C_{b1}) \quad (4)$$

where k_b is a constant representing the rate of chemical binding of chlorides and $\bar{C}_{b1}$ is the limited value of chemically bound chloride at a given free chloride concentration and thus is the function of free chloride C_f. Since the chemical binding takes place very quickly, k_b could be any large number. As long as it is large enough the actual value of k_b will not affect the results. Note that the sink term $Q(C_{b1})$ takes functioning only when it is positive and vanishes when it becomes negative. Assume that the bound chloride can be expressed in terms of the free chloride by Freundlich isotherm as follows,

$$C_b = \beta \left(\frac{C_f}{C_{fb}}\right)^{\alpha} \tag{5}$$

where α and β are the constants, and C_{fb} is the concentration of free chloride ions at the exposed surface. Note that, only two fitting constants are required in the Freundlich isotherm. Herein, the use of C_{fb} in Eq.(5) is only for the purpose of unit conversion. The reversible bound chloride in the representative concrete thus can be expressed as,

$$C_{b2} = C_b - \bar{C}_{b1} = \beta \left(\frac{C_f}{C_{fb}}\right)^{\alpha} - \bar{C}_{b1} \tag{6}$$

Considering that the chemical binding is much faster than the physical binding, it is assumed that the chemical binding process takes first, followed by the physical binding process. Fig.2 illustrates the relationships between the free chloride, irreversible and reversible bound chlorides, while the exact curves are dependent on the values of α, β, C_{fb} and $C_{b1,\max}$.

Assume that the concrete pore solution is an idealised dilute solution. The chemical potential of chloride ions in the concrete pore solution may be written in terms of the concentration of chloride ions as follows,

$$\mu = \mu_o(T, P) + RTln(C_f + C_{b2}) \tag{7}$$

where μ is the chemical potential of chloride ions, μ_o is the standard chemical potential, T is the absolute temperature, P is the pressure, and R is the gas constant. The reason that the reversible bound chloride C_{b2} is also included in Eq.(7) is because the physically bound chloride still carries its charge although it is not able to move. Since the mass conservation of Eq.(3) is established based on the representative elementary volume of concrete that involves both the liquid and solid phases the reversible bound chloride that remains its charge will continue affecting the transport of free chloride ions. The driving force generated by the chemical potential gradient at a point defined by Eq.(7) applies to all charged chloride ions including the physically bound chloride. Under the action of the driving force, free chloride ions diffuse, whereas the physically bound chloride ions remain stationary due to the fact that the driving force they received is not enough to overcome their binding force. The flux of the free chloride ions caused by the chemical potential gradient described by Eq.(7) can be expressed as follows,

$$J = -\nu C_f \nabla\mu = -\nu RT \frac{C_f}{C_f + C_{b2}} \nabla\left(C_f + C_{b2}\right) = -D_e \frac{C_f}{C_f + C_{b2}} \nabla\left(C_f + C_{b2}\right) \tag{8}$$

where ν is the mobility constant and $D_e = \nu RT$ is the diffusion coefficient of chloride ions. Note that, if C_{b2} is linearly proportional to C_f, then Eq.(8) will reduce to the Fick's first law,

$$J = -D_e \nabla C_f \tag{9}$$

However, when a nonlinear binding isotherm is used for the physically bound chloride, the flux calculated from Eq.(8) is different from that calculated from Eq.(9). Eq.(8) indicates that the free chloride ions move from a place with higher overall concentration (C_f+C_{b2}) to a place with

lower overall concentration (C_f+C_{b2}), even when the free chloride concentration is lower in the former than in the latter (see the graphical illustration shown in Fig.3).

Note that, according to Eq.(3) all chlorides are defined based on the unit volume of representative elementary concrete. Thus, their units should be the mole or mass per unit volume of concrete. However, according to the steady-state diffusion tests, the unit used for chloride concentration in Eq.(8) or (9) is the unit of mole or mass per unit volume of pore solution [37] although the flux is defined as the mole or mass pass through per unit area of concrete in the unit time. In other words, if the flux unit used in Eq.(8) or (9) is consistent with what is used in Eq.(3), the concentration unit of chloride ions used in Eq.(8) or (9) have to be converted from the mole or mass of per unit volume of solution to the mole or mass of per unit volume of concrete. By doing so, the right-hand-side term of Eq.(8) and Eq.(9) need to be divided by concrete porosity ε. Substituting Eqs.(4), (5), (6) and (8) into (3), it yields,

$$\left(1+\frac{dC_{b2}}{dC_f}\right)\frac{\partial C_f}{\partial t}=\nabla\left[\frac{D_e}{\varepsilon}\frac{C_f}{C_f+C_{b2}}\left(1+\frac{dC_{b2}}{dC_f}\right)\nabla C_f\right]-k_b(\bar{C}_{b1}-C_{b1}) \quad (10)$$

Eq.(10) can be used to calculate the free chloride content in concrete if its initial and boundary conditions are known, in which C_{b1} and C_{b2} are calculated using Eqs.(4) and (6), respectively, and $\bar{C}_{b1}$ is taken as $\beta\left(\frac{C_f}{C_{fb}}\right)^{\alpha}$ or $C_{b1,max}$, whichever is smaller (see Fig.2). Eq.(10) can be solved numerically, for example, by using the PDEPE scripts built in the Matlab. The total chloride content can be calculated as follows,

$$C_T=C_f+C_{b1}+C_{b2} \quad (11)$$

4. Numerical examples

The above-described chloride diffusion model with considering chloride binding is applied to reproduce the experimentally obtained chloride profiles in three different types of concrete. The first experiment is the OPC concrete mixed with type 50 cement (370 kg/m^3), graded silica sand (738 kg/m^3), crushed limestone aggregate (1107 kg/m^3), water (148 kg/m^3), and superplacticizer (4.64 kg/m^3), immersed in a multi-component ionic solution with ionic concentration (wt% of bath) of potassium 4.68%, chloride 16.82%, sulphate 0.18%, calcium 0.134%, magnesium 0.107%, and sodium 7.76%, for 3, 6 and 12 months [38]. The parameters employed in the present simulation are diffusion coefficient D_e/ε=1.05x10^{-11} m^2/s, surface concentration of free chloride C_{fb}=0.8 (%wt of concrete), binding constants α=2/3, β=0.9C_{fb}, and maximum irreversible bound chloride $C_{b1,max}$=0.5β. Fig.4 plots the diffusion profiles of chlorides for both the free and total chlorides obtained from the present simulation at the exposure times of 3, 6 and 12 months. The comparison between the simulated total chloride and experimentally obtained total chloride is shown in Fig.4b. It can be seen from the concentration profiles of free chloride shown in Fig.4a that the chloride penetration becomes slower with the increased time. The predicted total chlorides from the present simulation are reasonably in good agreement with the experimental data. The deviation of the few experimental data points from the simulation curves might be due to the randomness of the experiments. Overall, the simulated curves provide very good tendency of chloride movement. This indicates that the present model is able to represent the main transport features of chlorides

in concrete. It was reported that if the Fick's second law alone is used to model the chloride transport, the diffusion coefficient calculated from the experimentally measured total chlorides varies from $2.88x1.0^{-12}$ m^2/s to $2.12x1.0^{-11}$ m^2/s [38], the variation of which is almost about 10 time.

The second experiment is the 50% pulverized fuel ash (PFA) concrete mixed with grade 40 normal cement (398 kg/m^3), PFA (398 kg/m^3), fine aggregate (1194 kg/m^3), coarse aggregate (669 kg/m^3), and water (175 kg/m^3), immersed in a 5 M sodium-chloride solution at 20 ^oC for 3, 6 and 12 months [39]. The parameters employed in the present simulation are diffusion coefficient $D_e/\varepsilon=0.625x10^{-11}$ m^2/s, surface concentration of free chloride $C_{fb}=0.6$ (%wt of concrete), binding constants $\alpha=2/3$, $\beta=0.65C_{fb}$, and maximum irreversible bound chloride $C_{b1,max}=0.5\beta$. The use of a lower diffusion coefficient and a lower binding capacity for PFA concrete is mainly due to the fineness and spherical shape of PFA particles, which improve the pore-microstructure of mixed concrete. Fig.5 plots the diffusion profiles of chlorides for both the free and total chlorides obtained from the present simulation at the exposure times of 3, 6 and 12 months. Again, it can be seen from the figure that, the speed of chloride penetration decreases with the increased time. It is evident from the comparison shown in the figure that the predicted total chlorides are in good agreement with the experimental data, although there is one experimental data point, which is deviance from the simulated curves. If it is to use the Fick's second law alone to model the chloride transport, one has to use the concentration- or time-dependent chloride diffusion coefficient in order to achieve a decent fit with the experimentally obtained chloride profiles at different times [39].

The third experiment is the concrete mixed with 75% Portland cement (364 kg/m^3), 25% fly ash (122 kg/m^3), sand (588 kg/m^3), coarse aggregate (1142 kg/m^3), and water (145.6 kg/m^3), immersed in a 3.5% sodium-chloride solution for 90 days [40,41]. The parameters employed in the present simulation are diffusion coefficient $D_e/\varepsilon=0.25x10^{-11}$ m^2/s, surface concentration of free chloride $C_{fb}=0.22$ (%wt of concrete), binding constants $\alpha=2/3$, $\beta=0.7C_{fb}$, and maximum irreversible bound chloride $C_{b1,max}=0.5\beta$. Fig.6 shows the comparison between the simulation results and experimentally measured data for both the free and total chlorides. Again, good agreement can been seen between the numerical and experimental results. It was reported that, if the Fick's second law alone is used to model the chloride transport, the diffusion coefficient was found to be $0.26x10^{-11}$ m^2/s for the free chloride and $0.729x10^{-11}$ m^2/s for the total chloride [41].

5. Conclusions

In this paper, we have presented a new chloride diffusion model in concrete exposed to marine environment, which considers the individual effects of the physically and chemically bound chlorides. In the present model the chemical binding of chlorides is assumed to be irreversible and is described by using a sink term in the mass conservation equation; whereas the physical binding of chlorides is assumed to be reversible and is treated by using a binding isotherm. Unlike most existing chloride binding models in which the charge of the physically bound chloride is ignored, the present model takes into account the effect of its charge on the transport

of free chloride ions. Finally, the mass conservation of the total chlorides in concrete is established based on the unit volume of representative elementary concrete, which provides a consistent and concise description for each involved component. The comparison of the free and/or total chloride profiles predicted by using the present model and those measured in experiments has demonstrated the capability and rationality of the present model.

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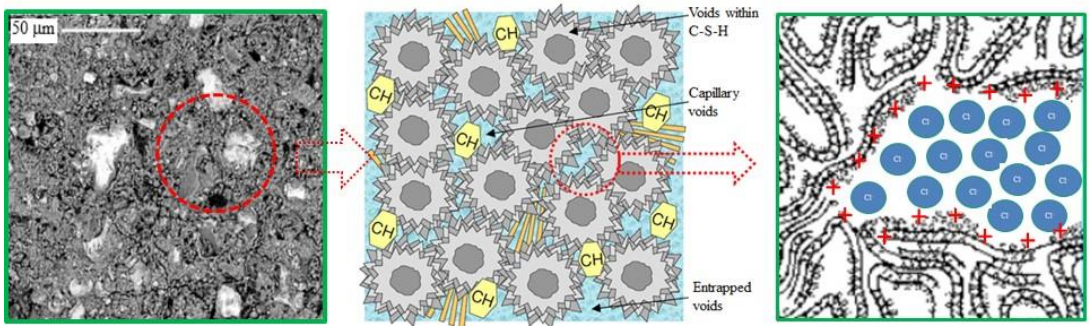


Fig.1 (a) Schematic of a representative elementary volume of concrete. (b) Pore micro-structure. (c) Surface charge and chloride ions in pore solution.

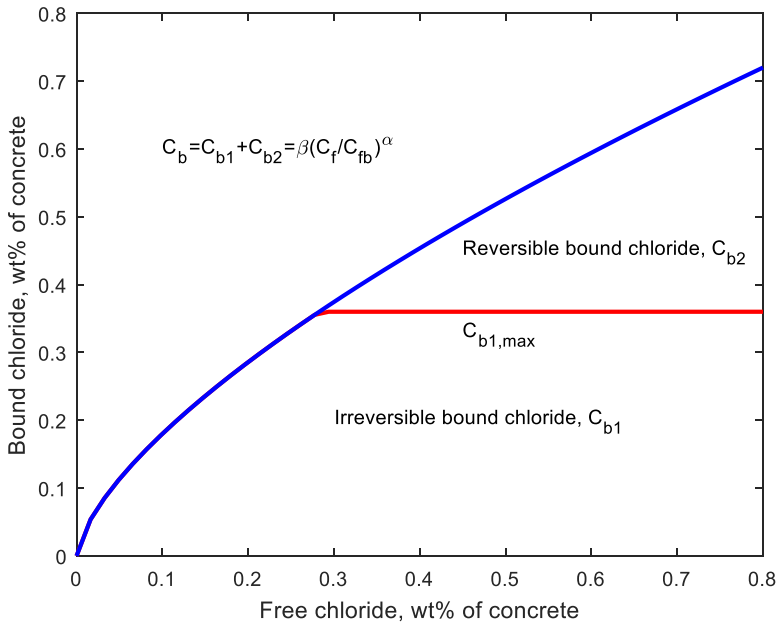


Fig.2 Illustration of irreversible (C_{b1}) and reversible (C_{b2}) bound chlorides.

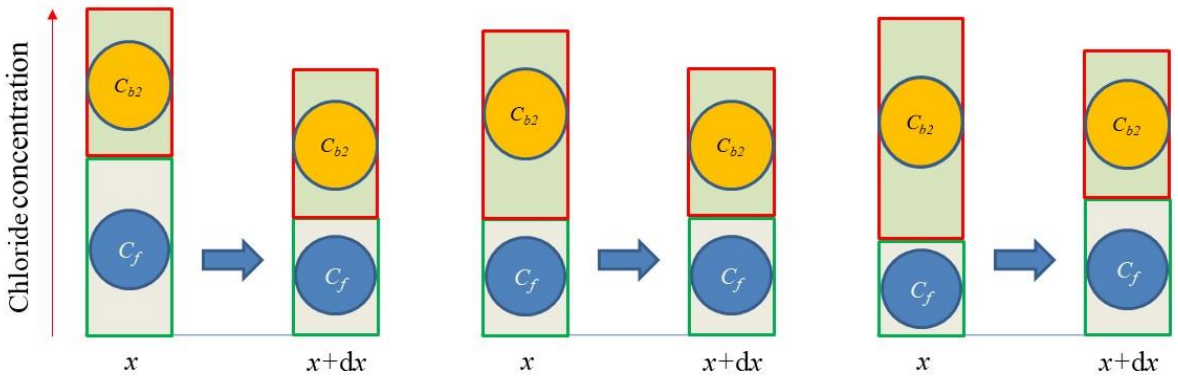


Fig.3 Free chloride diffusion direction in three cases of $C_f(x)+C_{b2}(x)>C_f(x+dx)+C_{b2}(x+dx)$. (a) $C_f(x)>C_f(x+dx)$. (b) $C_f(x)=C_f(x+dx)$. (c) $C_f(x)<C_f(x+dx)$.

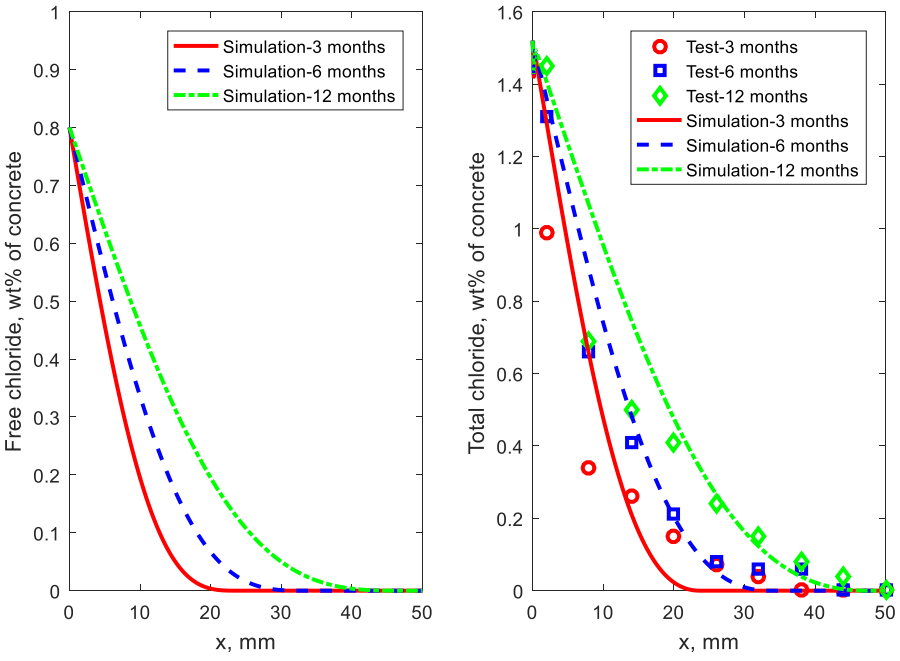
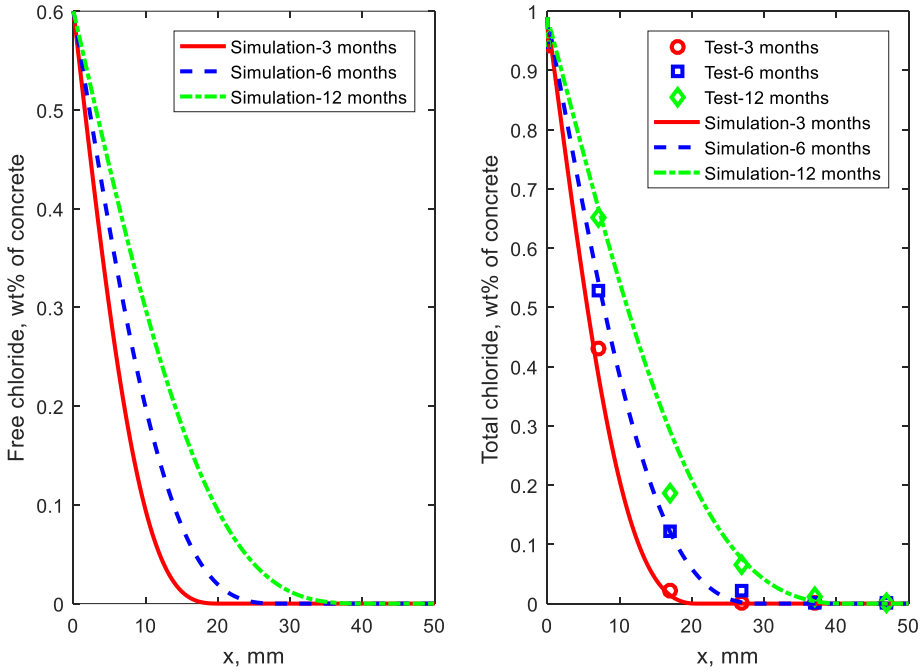


Fig.4 Free and total chlorides obtained from simulation and the comparison with experimental results [28]. (a) Free chloride profiles and (b) total chloride profiles.



(a) (b)

Fig.5 Free and total chlorides obtained from simulation and the comparison with experimental results [29]. (a) Free chloride profiles and (b) total chloride profiles.

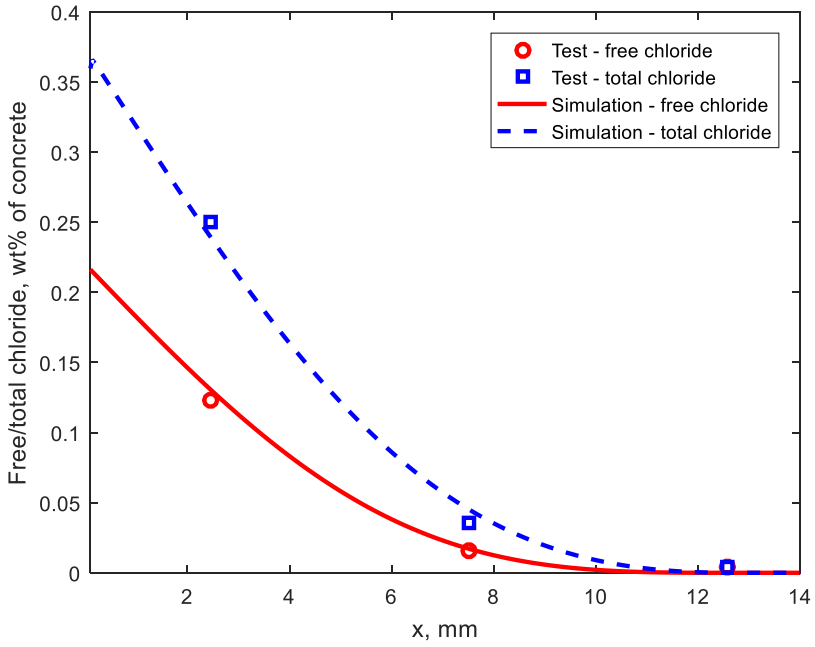


Fig.6 Comparison of free and total chlorides between simulations and experiments for 0.75PC+0.25FA concrete exposed to 3.5% NaCl solution for 90 days.